

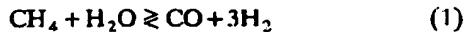
# Sorption-Enhanced Reaction Process for Hydrogen Production

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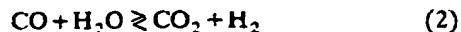
*A novel concept called Sorption Enhanced Reaction Process (SERP) for hydrogen production by steam-methane reformation (SMR) reaction uses a fixed packed column of an admixture of an SMR catalyst and a chemisorbent to remove carbon dioxide selectively from the reaction zone. The chemisorbent is periodically regenerated by using the principles of pressure swing adsorption. The SERP process steps allow direct production of high-purity hydrogen (> 95 mol %) at high methane to hydrogen conversion (> 80%) with dilute methane (< 5 mol %) and trace carbon oxide (~ 50 ppm) impurities at the reaction pressure by operating the reactor at a low temperature of 450°C. A conventional plug-flow reactor packed with catalyst alone not only needs to be operated at a much higher temperature (> 650°C) to achieve the same methane to hydrogen conversion, but produces a much lower purity of hydrogen product (~ 75 mol %) with a large quantity of carbon oxide (~ 20 mol %) impurities. A novel chemisorbent, which reversibly sorbs carbon dioxide in the presence of excess steam at a temperature of 300–500°C, was developed for application in the SERP and the process is experimentally demonstrated in a bench-scale apparatus.*

## Introduction

The most common industrial process for production of hydrogen uses the endothermic steam-methane reformation (SMR) reaction (Leiby, 1994)



It is generally carried out in a catalytic (Ni on alumina) reactor at a pressure of 50–600 psig and a temperature of 750–900°C. The reactor feed gas is a mixture of steam and methane (natural gas) in the ratio of 2.5–6.0. The reactor effluent gas typically contains 70–72% H<sub>2</sub>, 6–8% CH<sub>4</sub>, 8–10% CO, and 10–14% CO<sub>2</sub> on a dry basis. This gas is cooled in a waste heat boiler (steam produced) and fed to another catalytic (Fe or Cu on alumina) reactor for the exothermic water-gas shift (WGS) reaction (Leiby, 1994)



The high temperature WGS reactor is generally operated at a temperature of 300–400°C. The effluent gas from the reactor typically contains 71–75% H<sub>2</sub>, 4–7% CH<sub>4</sub>, 1–4% CO and 15–20% CO<sub>2</sub> on a dry basis. The effluent is further cooled to a temperature of 20–50°C (more steam is produced and water is condensed) and fed to a multicolumn pressure swing adsorption (PSA) process at a pressure of 50–600 psig. The PSA feed gas is saturated with water. The PSA process produces a hydrogen product stream containing dry 98–99.999+% H<sub>2</sub> at the feed gas pressure with a H<sub>2</sub> recovery of 70–90%. The waste gas from the PSA process containing unrecovered H<sub>2</sub> and all of feed H<sub>2</sub>O, CH<sub>4</sub>, CO and CO<sub>2</sub> is produced at a pressure of 2–10 psig, and it is used as part of the fuel required to supply the heat of the endothermic SMR reaction. Natural gas provides the balance of the required fuel. Figure 1 shows a block diagram for the above described SMR-WGS-PSA process train for production of pure H<sub>2</sub> (Leiby, 1994).

A multicolumn PSA process containing 4–12 adsorption beds is generally used (Wagner, 1969; Fuderer and Rudelstorfer, 1976; Sircar and Kratz, 1988) in conjunction with a

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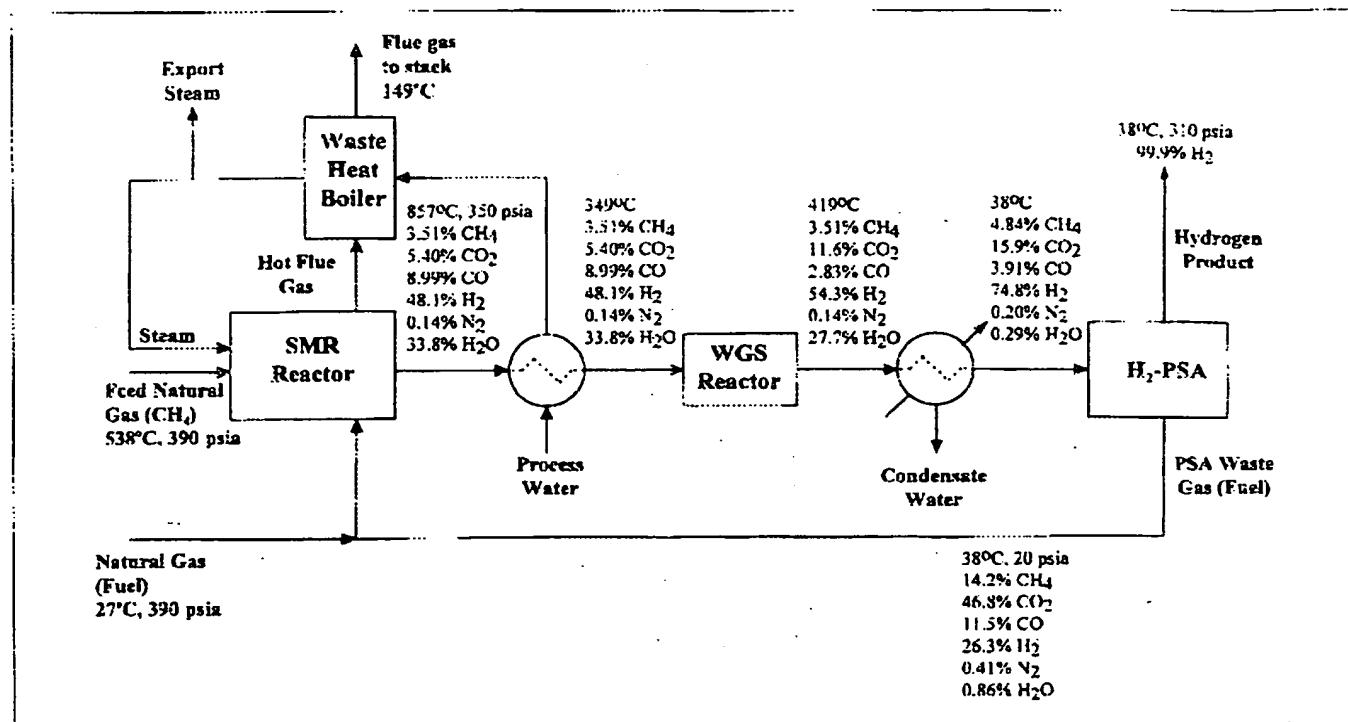


Figure 1. Conventional SMR process for hydrogen production.

combination of various PSA process steps (adsorption, cocurrent depressurization, countercurrent depressurization and purge, vacuum purge, cocurrent and countercurrent pressure equalization, feed and product pressurization, and so on). The net H<sub>2</sub> recovery from the PSA process and its adsorbent inventory depend on many variables like feed gas pressure and composition; design; operating conditions and cycle times of the PSA process steps; H<sub>2</sub> product purity; and so on. In particular, the CO and CO<sub>2</sub> concentrations of the feed gas are critical in determining the design and efficiency of separation of the PSA process because bulk CO<sub>2</sub> is difficult to desorb and dilute CO is difficult to adsorb.

The heat of reaction is supplied to the SMR reactor by combusting fresh natural gas and H<sub>2</sub>-PSA waste gas. The radiant thermal efficiency of the SMR reactor is typically 40–50%. The overall thermal efficiency of the SMR H<sub>2</sub> production unit, on the other hand, is about 85%. This is achieved by recovering waste heat from the reformer flue gas at the cost of additional heat-transfer equipment. The excess heat is partly recovered in the form of steam and the excess steam (over what is needed for SMR reaction) is often exported from the hydrogen production site.

The high-temperature operation of the SMR reactor, the catalyst deactivation due to coking, the use of high-temperature metallurgy for construction of the SMR reactor, the requirement of large interstage heat recovery systems, and the complex design of the multicolumn H<sub>2</sub>-PSA system significantly raises the capital cost of H<sub>2</sub> production. Nevertheless, the SMR-WGS-PSA process described by Figure 1 remains the most cost-effective method for production of pure H<sub>2</sub> in the commercial scale (1–100 MM SCFD H<sub>2</sub>). The technology

has been improved during the last 60 years through numerous innovations in the areas of natural gas desulfurization, SMR and WGS catalysis, reactor design, heat supply and removal systems, PSA process design and adsorbents, process control, heat generation and management, and so on. It will be extremely desirable if newer concepts for production of H<sub>2</sub> by SMR can be developed which reduce the capital cost compared to the conventional route.

In previous publications (Sircar et al., 1995; Carvill et al., 1996), we described a concept called Sorption Enhanced Reaction Process (SERP) which can yield high conversion of reactants to products for an equilibrium-controlled, endothermic reaction at a much lower temperature than would be necessary by a conventional catalytic reactor due to thermodynamic limits. The concept is based on Le Chatelier's principle that (a) the conversion of reactants to products and (b) the rate of forward reaction in an equilibrium controlled reaction can be increased by selectively removing some of the reaction products from the reaction zone. The SERP uses a selective adsorbent (admixture with the catalyst in the reactor) for selective removal of a reaction product and the adsorbent is periodically regenerated (absorbed component is desorbed) by using the principles of PSA. A specific design of the PSA cycle and a specific method of its operation makes the SERP concept very efficient by (a) directly producing the desired reaction product at high purity and conversion at reaction pressure, (b) permitting the operation of the reactor at a much lower temperature (cheaper metallurgy and heat exchange equipment), and (c) drastically reducing or eliminating the subsequent product purification requirements (cheaper product purification). The concept was demon-

strated experimentally for the production of pure CO by reacting CO<sub>2</sub> and H<sub>2</sub> (reverse water gas shift reaction according to Eq. 2) using a commercial WGS catalyst and NaX zeolite as the adsorbent for selective removal of a reaction product (H<sub>2</sub>O) from the reaction zone (Carvill et al., 1996). The purpose of this article is to demonstrate the applicability of SERP concept for the production of H<sub>2</sub> by SMR.

### Steam Methane Reforming

Both SMR and WGS reactions take place in the SMR reactor. The thermodynamic equilibrium constants (K) for these reactions, which are functions of reaction temperature only, may be written as

$$K_{\text{SMR}}(T) = \frac{P^2(y_{\text{H}_2})^3(y_{\text{CO}})}{(y_{\text{CH}_4})(y_{\text{H}_2\text{O}})} \quad (3)$$

$$K_{\text{WGS}}(T) = \frac{(y_{\text{CO}_2})(y_{\text{H}_2})}{(y_{\text{CO}})(y_{\text{H}_2\text{O}})} \quad (4)$$

Equations 3 and 4 describe the equilibrium relationships between gas-phase mole fractions of component *i* (CH<sub>4</sub>, CO, CO<sub>2</sub>, H<sub>2</sub>O and H<sub>2</sub>) in a batch reactor at a total gas phase pressure *P* and temperature *T*. They can be rearranged to obtain

$$y_{\text{H}_2} = \frac{[K_{\text{SMR}} K_{\text{WGS}}]^{0.25}}{[P]^{0.5}} \cdot \frac{[Y_{\text{CH}_4}]^{0.25} [Y_{\text{H}_2\text{O}}]^{0.5}}{[Y_{\text{CO}_2}]^{0.25}} \quad (5)$$

$$y_{\text{CO}} = \frac{[K_{\text{SMR}}]^{0.25}}{[K_{\text{WGS}}]^{0.75} [P]^{0.5}} \cdot \frac{[Y_{\text{CH}_4}]^{0.25} [Y_{\text{CO}_2}]^{0.75}}{[Y_{\text{H}_2}]^{0.5}} \quad (6)$$

Equation 5 shows that the gas-phase H<sub>2</sub> mole fraction can be increased by decreasing the corresponding CO<sub>2</sub> mole fraction. Equation 6 shows that the gas-phase CO mole fraction decreases as the corresponding CO<sub>2</sub> mole fraction decreases. More importantly, these equations show that a very high conversion of CH<sub>4</sub> to H<sub>2</sub> can be achieved in a SMR reactor even at a moderate temperature (low K<sub>SMR</sub>) if CO<sub>2</sub> is removed from the reaction zone. At the same time, the co-production of CO will be suppressed.

Figure 2 shows plots of K<sub>SMR</sub> and K<sub>WGS</sub> as functions of *T* (Twigg, 1989). The equilibrium constants increase and decrease exponentially with increasing *T* for the SMR and WGS reactions, respectively. The figure also shows the batch conversion of CH<sub>4</sub> to H<sub>2</sub> as a function of *T* for a feed mixture containing a H<sub>2</sub>O/CH<sub>4</sub> ratio of 6:1 at a constant reactor pressure of 50 psig. The conversion decreases drastically as the reaction temperature falls below 650°C. These conversion numbers were calculated by simultaneously solving Eqs. 3 and 4 with the appropriate mass balance equations for a constant pressure and a constant temperature batch reactor system.

We now examine a constant temperature (*T*) and constant pressure (*P*) batch SMR reactor where the CO<sub>2</sub> produced by reactions 1 and 2 is selectively removed from the gas phase by adsorption. It can be shown that the equilibrium gas-phase

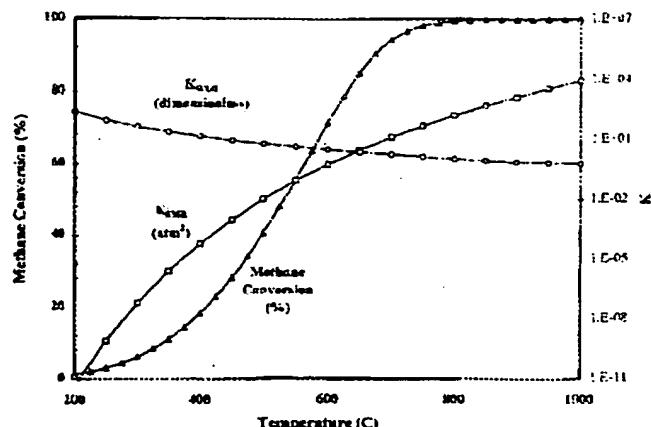


Figure 2. Temperature dependence of equilibrium constants for SMR and WGS reactions, and batch conversions of CH<sub>4</sub> to H<sub>2</sub> for a 6:1 H<sub>2</sub>O/CH<sub>4</sub> reactor feed at 50 psig (445.8 kPa).

mole fractions in such a system are given by

$$y_{\text{H}_2} = \frac{(3\beta + \delta)}{(1 + 2\beta - f\delta)}; \quad y_{\text{CH}_4} = \frac{1 - \beta(1 + \alpha)}{(1 + \alpha)(1 + 2\beta - f\delta)}; \\ y_{\text{H}_2\text{O}} = \frac{\alpha - (\beta + \delta)(1 + \alpha)}{(1 + \alpha)(1 + 2\beta - f\delta)}; \quad y_{\text{CO}} = \frac{(\beta - \delta)}{(1 + 2\beta - f\delta)}; \\ y_{\text{CO}_2} = \frac{(1 - f)\delta}{(1 + 2\beta - f\delta)} \quad (7)$$

where  $\alpha$  is the molar ratio of feed H<sub>2</sub>O/CH<sub>4</sub> introduced into the batch reactor at *P* and *T*,  $\beta$  is the moles of CO produced by the SMR reaction per mole of the feed gas,  $\delta$  is the moles of CO reacted by the WGS reaction per mole of the feed gas, and  $f$  is the fraction of CO<sub>2</sub> produced by the WGS reaction that is removed from the gas phase by adsorption. The variables  $\alpha$ ,  $\beta$ , and  $\delta$  are related by the thermodynamic equations.

$$K_{\text{SMR}}(T)$$

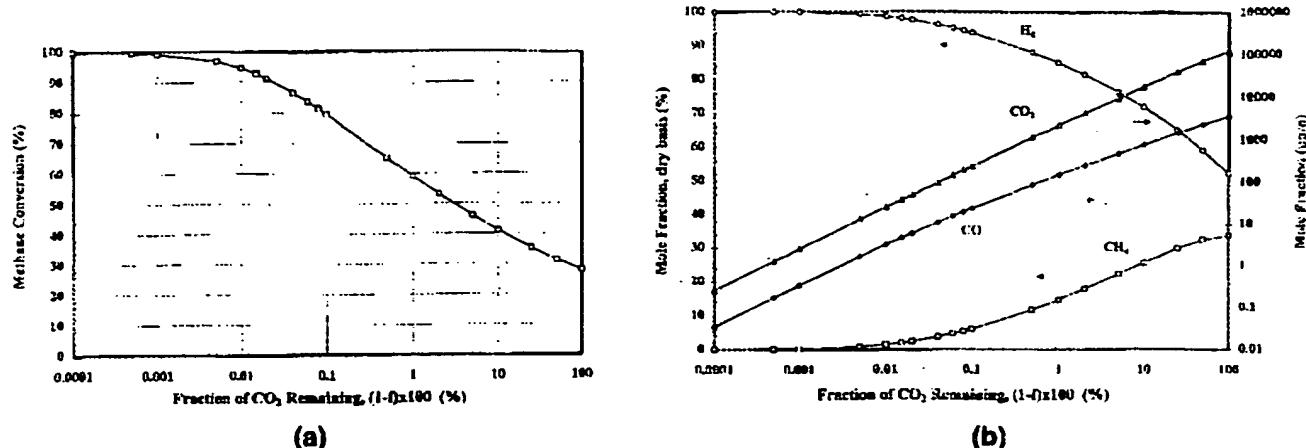
$$= \frac{P^2(\beta - \delta)(3\beta + \delta)^3(1 + \alpha)^2}{[1 + 2\beta - f\delta]^2[1 - \beta(1 + \alpha)][\alpha - (\beta + \delta)(\beta + \delta)]} \quad (8)$$

$$K_{\text{WGS}}(T) = \frac{(1 - f)\delta(3\beta + \delta)(1 + \alpha)}{(\beta - \delta)[\alpha - (\beta + \delta)(1 + \alpha)]} \quad (9)$$

The moles of H<sub>2</sub> formed per mole of CH<sub>4</sub> introduced into the reactor ( $\chi$ ) is given by

$$\chi = (3\beta + \delta)(1 + \alpha) \quad (10)$$

Equations 8 and 9 can be simultaneously solved for a given set of values of *P*, *T* and  $\alpha$  in order to calculate  $\beta$  and  $\delta$  as



**Figure 3. Performance of batch SMR reactor for a 6:1 H<sub>2</sub>O / CH<sub>4</sub> reactor feed at 450°C and 50 psig (445.8 kPa).**  
 (a) Equilibrium conversion of CH<sub>4</sub> to H<sub>2</sub> with CO<sub>2</sub> removal from reaction zone; (b) equilibrium gas phase composition with CO<sub>2</sub> removal from reaction zone.

functions of  $f$ . Then, Eqs. 7 and 10 can be used to calculate equilibrium gas-phase mole fractions of all components and the  $\text{CH}_4$  to  $\text{H}_2$  conversion ( $\approx \chi/4$ ) in the batch reactor as functions of  $f$ .

Figures 3a and 3b show the results of above described calculations for  $\alpha = 6:1$ ,  $P = 50$  psig, and  $T = 450^\circ\text{C}$ . Figure 3a plots the conversion of  $\text{CH}_4$  to  $\text{H}_2$  as a function of  $\ln(1-f)$ , and Figure 3b shows the corresponding dependence of gas-phase mole fractions (dry basis) as functions of  $\ln(1-f)$ . The conversion numbers depicted by Figure 2 can be obtained by setting  $f = 0$  in Eqs. 7-10. Figures 3a and 3b clearly demonstrate that (a) very high conversion of  $\text{CH}_4$  to  $\text{H}_2$  ( $> 80\%$ ) by the SMR-WGS reactions can be achieved at a moderate temperature of  $450^\circ\text{C}$ , and (b) a gas phase, which has a large  $\text{H}_2$  mole fraction ( $> 95\%$ ) and which is essentially free of carbon oxides ( $< 100$  ppm) on a dry basis, can be produced when 99.9% or more of the  $\text{CO}_2$  produced by the reactions is removed by the adsorbent. The corresponding  $\text{CH}_4$  to  $\text{H}_2$  conversion for the case where  $\text{CO}_2$  is not removed from the reaction zone is only 28.0% (Figure 2) and the equilibrium gas-phase mole fractions are 52.8%  $\text{H}_2$ , 33.8%  $\text{CH}_4$ , 12.9%  $\text{CO}_2$ , and 0.34%  $\text{CO}$  (dry basis). Thus, all the key advantages of the SERP concept described earlier can be realized for production of  $\text{H}_2$  by reacting  $\text{H}_2\text{O}$  and  $\text{CH}_4$  in a reactor packed with an admixture of SMR catalyst and a  $\text{CO}_2$  selective adsorbent.

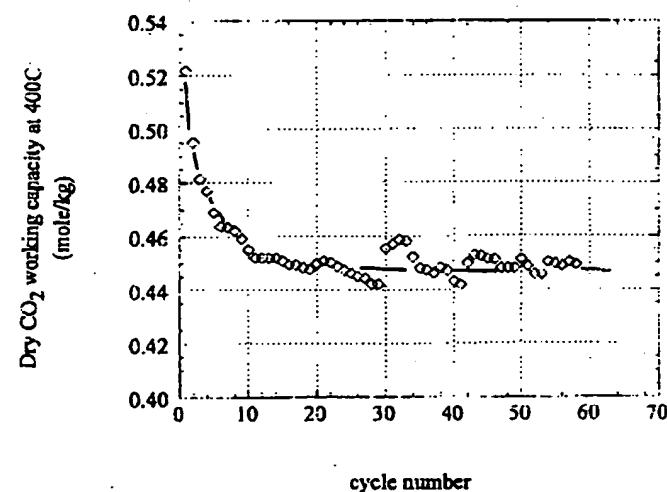
## CO<sub>2</sub> Adsorbent for H<sub>2</sub>-SERP

A key requirement for practical utilization of the SERP concept for  $H_2$  production by SMR is the availability of an adsorbent which can selectively remove  $CO_2$  from the SMR reaction zone at moderately high temperatures (300°–500°C) in the presence of a large partial pressure of steam. The other requirements are that (a) the adsorbent can be regenerated using the principles of PSA, (b) the adsorbent exhibits a substantial  $CO_2$  working capacity between the conditions of the adsorption and desorption steps of SERP, (c) the kinetics of ad(dc)sorption of  $CO_2$  is relatively fast, and (d) the material

is stable in presence of steam and has adequate mechanical strength.

To our best knowledge, there is no commercially produced adsorbent that satisfies the above requirements. So, we developed a proprietary material which reversibly chemisorbs  $\text{CO}_2$  in the temperature range of 300–500°C in the presence of excess steam (Anand et al., 1996; Hufton et al., 1998). The material is a potassium carbonate promoted hydrotalcite (pelletized form).

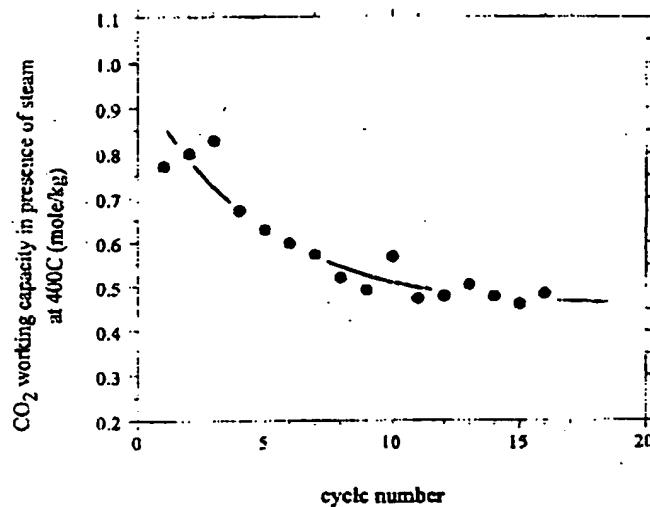
The reversible  $\text{CO}_2$  ad(de)sorption property of the proprietary chemisorbent is demonstrated by Figure 4. It plots the net  $\text{CO}_2$  working capacity at a temperature of  $400^\circ\text{C}$ . The data are generated by exposing the chemisorbent to a dry gas mixture containing  $\text{CO}_2$  (70%) and  $\text{N}_2$  (30%) at a total gas pressure of one atmosphere (adsorption) for a period of one



**Figure 4.** Dry  $\text{CO}_2$  working capacity on chemisorbent cycled between  $\text{CO}_2$  partial pressures of 0.7 and 0.0 atm at  $400^\circ\text{C}$  as functions of cycle number.

hour in a conventional micro balance followed by exposing the material to pure and dry  $N_2$  at a pressure of one atmosphere (desorption) for one hour (Anand et al., 1996). The difference in the weights of the material under these two conditions is defined as the net  $CO_2$  working capacity. This ad(de)sorption process was repeated over many cycles. Figure 4 plots the net  $CO_2$  working capacity as a function of the cycle numbers. It shows that a stable reversible  $CO_2$  working capacity of  $\sim 0.45$  mol/kg is achieved by the material after 10 cycles of operation. The  $CO_2$  working capacity decreases during the first 10 cycles indicating that a certain portion of  $CO_2$  is irreversibly chemisorbed on the material.

The net  $CO_2$  working capacity of the material in the presence of steam was measured by flowing a gaseous mixture of  $CO_2$  and  $H_2O$  ( $CO_2$  partial pressure of 0.3 atm and steam partial pressure of 10 atm) at 400°C over the chemisorbent contained in a small thermostated chamber until the effluent gas  $CO_2$  concentration was equal to that of the feed gas. The chemisorbed  $CO_2$  was then desorbed by flowing dry  $CO_2$ -free  $N_2$  over the sample at 400°C and ambient pressure while monitoring the effluent gas-flow rate and its  $CO_2$  concentration. The net working  $CO_2$  capacity was estimated by the amount of  $CO_2$  desorbed. This ad(de)sorption experiment was also carried out over many cycles. Figure 5 shows the results. It may be seen that the  $CO_2$  working capacity for chemisorption on the material at 400°C in the presence of steam became practically constant after 10 cycles of exposure to  $CO_2$ -steam mixture indicating reversible chemisorption. Again, the  $CO_2$  working capacity decreased during the initial ad(de)sorption cycles due to some irreversible chemisorption. A comparison of the data in Figures 4 and 5 shows that the net reversible  $CO_2$  working capacity on the chemisorbent at 400°C is not affected by the presence of excess steam in the gas phase. The crush strengths of the pelletized chemisorbent were very similar before and after exposure to steam (Huston et al., 1998).



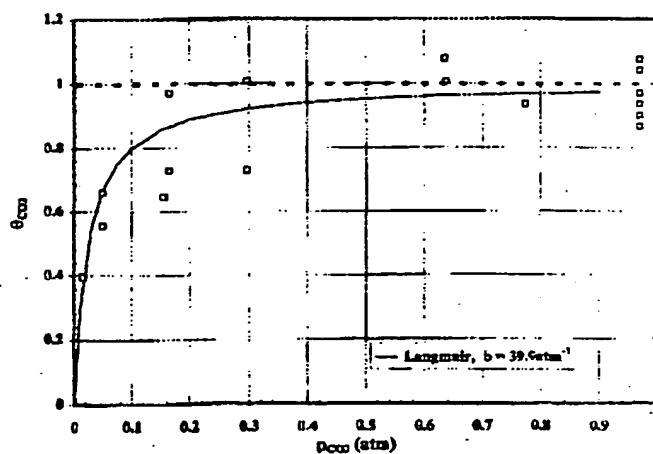
**Figure 5.**  $CO_2$  working capacity on chemisorbent cycled between  $CO_2$  partial pressures of 0.3 and 0.0 atm in presence of steam (partial pressure = 10 atm) at 400°C as functions of cycle number.

## Sorption Properties of the Chemisorbent

We measured the equilibrium isotherm, the kinetics, and the desorption characteristics for sorption of dry  $CO_2$  on the chemisorbent at 400°C using a column apparatus. It consisted of a stainless steel column (internal diameter = 1.1 cm; length = 205.7 cm) packed with 160 g of the chemisorbent (0.16-cm-diameter pellets). It was thermostated at 400°C using electric heaters. The column was initially filled with pure  $N_2$  at atmospheric pressure and 400°C. Preheated  $CO_2 + N_2$  mixtures containing different mole fractions of  $CO_2$  were then passed through the column at constant flow rates ( $Q^0$ ) at near ambient pressures. The effluent gas-flow rate [ $Q(t)$ ] and  $CO_2$  concentration [ $y(t)$ ] were monitored as functions of time ( $t$ ) until complete breakthrough of  $CO_2$  (effluent gas concentration is the same as that of feed) occurred. The  $CO_2$  was then desorbed by flowing pure  $N_2$  through the column at a constant flow rate ( $Q^0$ ) at near ambient pressure. The effluent gas-flow rate [ $Q(t)$ ] and its  $CO_2$  concentration [ $y(t)$ ] were again monitored as functions of time ( $t$ ). A continuous infrared  $CO_2$  (Beckman) analyzer was used for measurement of  $CO_2$  concentrations. The void volume in the column was measured by the conventional helium expansion technique. The experiments were conducted after repeatedly exposing the material to  $CO_2$  at 400°C and then regenerating it by  $N_2$  purge in order to saturate the column with irreversibly adsorbed  $CO_2$ .

The adsorption capacity of the chemisorbent at different partial pressures of  $CO_2$  ( $0 \leq p_{CO_2} \leq 1$ ) at 400°C were estimated by carrying out material balances in conjunction with the adsorption breakthrough data (Sircar and Kumar, 1983). Figure 6 shows an example of the reversible  $CO_2$  chemisorption isotherm on the material at 400°C. It plots the fractional coverage of  $CO_2$  ( $\theta$ ) as a function of equilibrium gas-phase  $CO_2$  partial pressure ( $p_{CO_2}$ ). The fractional coverage is defined by the ratio of actual amount of  $CO_2$  adsorbed to the saturation  $CO_2$  capacity. These data were measured using one batch of the material. The saturation capacity somewhat varied from batch to batch.

It may be seen from Figure 6 that the  $CO_2$  isotherm is rather steep in the low  $CO_2$  partial pressure region. The



**Figure 6.** Reversible sorption Isotherm of  $CO_2$  on chemisorbent at 400°C.

fractional coverage of  $\text{CO}_2$  approaches unity when  $p_{\text{CO}_2} \geq 0.3$ . This explains the similarity between the net  $\text{CO}_2$  working capacities of Figures 4 and 5 which were measured using  $p_{\text{CO}_2}$  values of 0.7 and 0.3, respectively. The chemisorption isotherm of Figure 6 is Type I in shape by Brunauer classification (Young and Crowell, 1962; Hayward and Trapnell, 1964), and it can be described by the Langmuir model ( $\theta = \frac{bp_{\text{CO}_2}}{1 + bp_{\text{CO}_2}}$ ) where  $b$  is the Langmuir gas-solid interaction parameter. The solid line of Figure 6 gives the best fit of the data [ $b = 39.9 \text{ atm}^{-1}$ ] by the model.

Figure 7 shows an example of  $\text{CO}_2$  adsorption breakthrough data on the material at  $400^\circ\text{C}$ . It was generated by using a  $\text{CO}_2$  feed gas mole fraction of 0.657 ( $y^0$ ) at a feed mass-flow rate of  $3.0 \times 10^{-5} \text{ gmol/cm}^2/\text{s}$  (based on empty cross-section of column). The figure plots the dimensionless effluent gas concentrations [ $y(t)/y^0$ ] as functions of dimensionless times ( $t/t^0$ ), where  $t^0$  is the stoichiometric breakthrough time for local equilibrium case (Sircar and Kumar, 1983). It shows that the breakthrough curve is almost a step function at dimensionless time of unity which indicates that the kinetics of chemisorption of  $\text{CO}_2$  on the material is very fast at  $400^\circ\text{C}$ .

Figure 8 shows an example of the  $\text{CO}_2$  desorption profile from the chemisorbent (saturated with 65.7%  $\text{CO}_2 + 34.3\%$   $\text{N}_2$  at ambient pressure) by purge with  $\text{N}_2$  at  $400^\circ\text{C}$ . The  $\text{N}_2$  inlet gas mass-flow rate was  $3.0 \times 10^{-5} \text{ gmol/cm}^2/\text{s}$ . It plots the fraction of  $\text{CO}_2$  desorbed [ $F = N_{\text{CO}_2}(t)/N^0_{\text{CO}_2}$ ] as a function of total effluent gas quantity [ $N(t) = \int_0^t Q(t) \cdot dt$ ] at any time  $t$ . The quantity  $N_{\text{CO}_2}(t) [= \int_0^t Q(t) \cdot y(t) dt]$  is the amount of  $\text{CO}_2$  desorbed from the column at time  $t$ .  $N^0_{\text{CO}_2}$  is the total amount of  $\text{CO}_2$  in the column at the start of the desorption test. These quantities were calculated from the experimental desorption effluent gas profiles. The  $\text{CO}_2$  desorption characteristics exhibited by Figure 8 are typical for an adsorbate with reversible Type I adsorption isotherm (Sircar and Golden, 1995). We used the isothermal, local equilibrium model for desorption of a Langmuirian sorbate by purge (Sircar and Golden, 1995; Sircar and Kumar, 1985) to describe the data of Figure 8 using the isotherm of Figure 6. The solid line in Figure 8 shows the results. The excellent fit

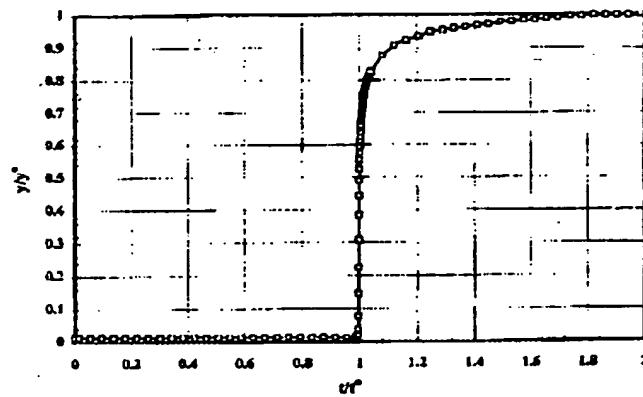


Figure 7. Column breakthrough characteristics for  $\text{CO}_2$  on chemisorbent at  $400^\circ\text{C}$  using a feed gas containing 65.7%  $\text{CO}_2$  and 34.3%  $\text{N}_2$  at ambient pressure.

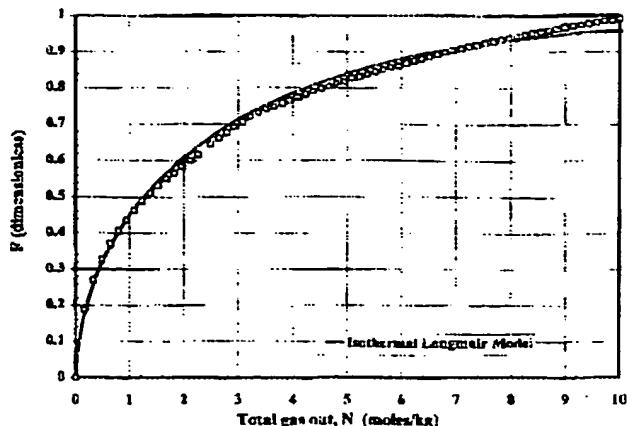


Figure 8.  $\text{CO}_2$  desorption characteristics by  $\text{N}_2$  purge for chemisorbent saturated with 65.7%  $\text{CO}_2$  and 34.3%  $\text{N}_2$  at ambient pressure and  $400^\circ\text{C}$ .

of the desorption data by the model indicates that  $\text{CO}_2$  desorption by purge from the material is essentially local-equilibrium controlled.

The above results indicate that the proprietary material exhibits all of the desirable properties (reversible and substantial  $\text{CO}_2$  sorption capacity in presence of steam, fast kinetics, desorption of  $\text{CO}_2$  by pressure reduction and purge with a nonadsorbing gas) required for use by the SERP concept.

### SERP for Hydrogen Production

The cyclic steps of the Sorption Enhanced Reaction Process for production of  $\text{H}_2$  by SMR are as follows (Carvill et al., 1996):

(a) *Sorption-Reaction Step:* Flow mixture of steam and methane at a reaction temperature ( $T_R$ ) and pressure ( $P_R$ ) through a tubular catalytic reactor packed with an admixture of a  $\text{CO}_2$  chemisorbent and a SMR catalyst. A hydrogen enriched effluent gas containing primarily  $\text{H}_2$  and  $\text{CH}_4$  at pressure  $P_R$  is produced. A part of this effluent gas is withdrawn as the  $\text{H}_2$  enriched product gas. The step is continued until the carbon oxide and methane concentrations of the effluent gas reach a preset level (say  $\sim 50 \text{ ppm}$  and 5%, respectively).

(b) *Depressurization Step:* The reactor-adsorber is depressurized in a direction countercurrent to that of the feed gas flow from pressure  $P_R$  to a pressure of  $P_D$ . A gas mixture containing  $\text{H}_2\text{O}$ ,  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and  $\text{CH}_4$  (primarily interparticle-void gas and some desorbed  $\text{CO}_2$ ) is produced. The pressure  $P_D$  can be atmospheric or subatmospheric.

(c) *Purge I Step:* The reactor-adsorber is then purged in a direction countercurrent to that of the feed gas flow at pressure  $P_D$  with a relatively nonadsorbing gas (such as  $\text{CH}_4$  or steam). The effluent gas contains the major part of the desorbed  $\text{CO}_2$  from the chemisorbent.

(d) *Purge II Step:* The reactor-adsorber is purged in a countercurrent direction with a part of the  $\text{H}_2$  enriched effluent gas produced during step a. The purge effluent gas primarily contains a mixture of  $\text{H}_2\text{O}$ ,  $\text{CH}_4$ ,  $\text{CO}_2$  and  $\text{H}_2$ .

(e) *Pressurization Step:* The reactor adsorber is then repressurized from  $P_D$  to  $P_R$  countercurrently with a part of

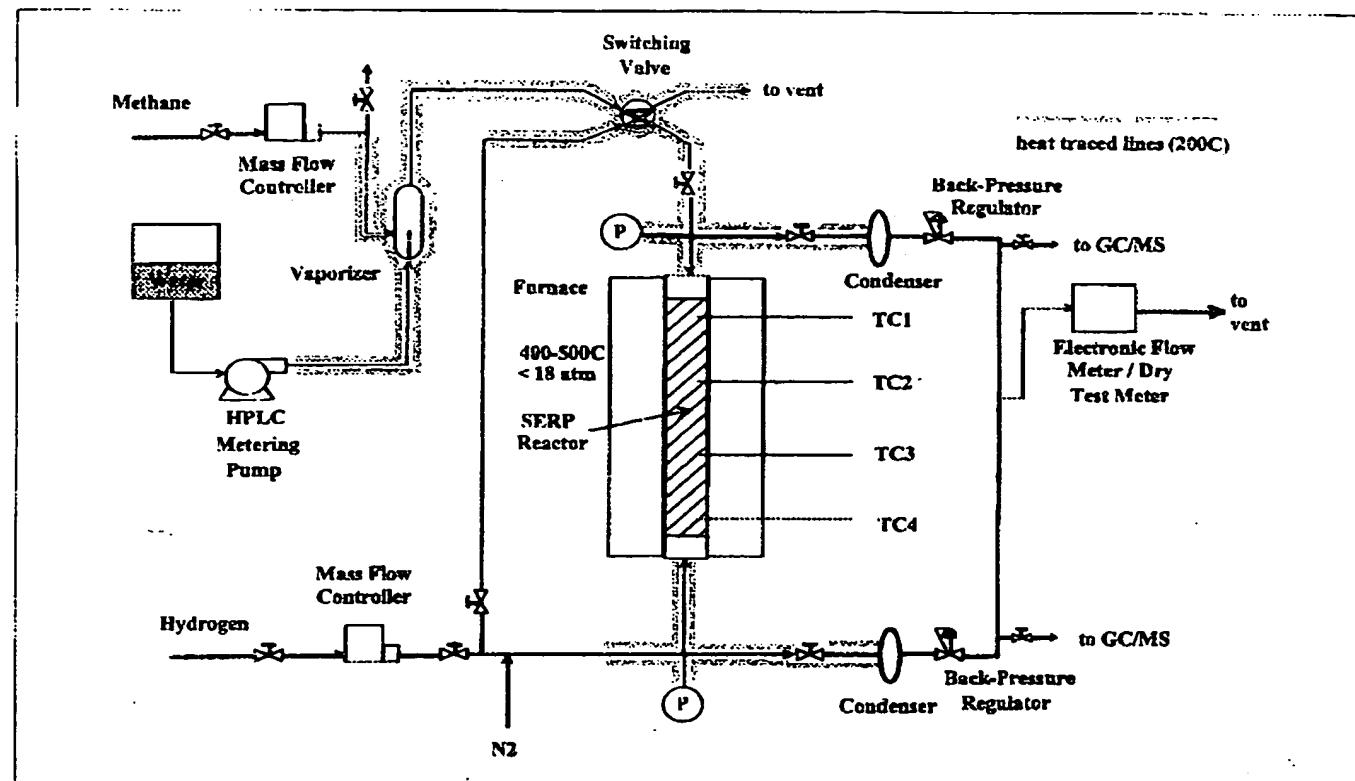


Figure 9. Bench-scale apparatus for testing SERP concept for  $H_2$  production.

the  $H_2$  enriched product gas from step a. The cycle then restarts from step a.

At least two parallel adsorber-reactors are needed by SERP to sustain continuous feed and product gas flows. The cycle times for the steps of the process are such that when one reactor carries out step a, the other reactor goes through steps b-c. The reactors are maintained near isothermal conditions at  $T_R$  by indirectly supplying heat of reaction and desorption through the reactor walls.

#### Bench-Scale Testing of SERP for $H_2$ Production

The single reactor, bench-scale apparatus described in our previous article (Carvill et al., 1996) was retrofitted to operate SERP for  $H_2$  production. Figure 9 shows the modified apparatus. The stainless steel reactor (internal diameter = 3.8 cm; length = 106.7 cm) was packed with the admixture of proprietary  $CO_2$  chemisorbent and a commercial SMR catalyst (1:1 weight ratio). The total amount of sorbent + catalyst in the reactor was 1.86 kg. The particle diameters of both the sorbent and the catalyst were  $\sim 0.3$  cm. Liquid water was vaporized and mixed with  $CH_4$  to form the SMR feed gas.  $N_2$  at ambient pressure was used as the purge gas for step c. The reactor temperature was maintained at  $450 \pm 10^\circ C$  during the steps of the process. The analytical instruments used in the apparatus are described in Figure 9 and elsewhere (Carvill et al., 1996).

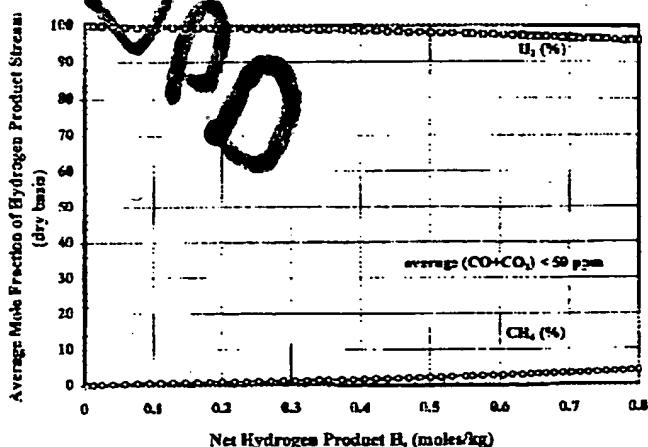
The apparatus was designed to evaluate the performance of the individual steps of the SERP in a sequential manner. It was not run continuously.

#### SERP Column Test Data

An experiment was carried out according to the previously described SERP concept using the apparatus of Figure 9. The feed gas contained a steam:methane mixture in the ratio of 6:1 at a pressure of 55 psig (480.3 kPa) ( $P_R$ ) and at a temperature of  $450^\circ C$  ( $T_R$ ). The feed gas-flow rate was  $3.0 \times 10^{-5}$  g mol/cm<sup>2</sup>/s. The purge gas pressure was  $\sim 2$  psig ( $\sim 115.1$  kPa) ( $P_D$ ). The reactor was initially pressurized with  $H_2$  at 55 psig (480.3 kPa) and  $450^\circ C$ . The quantity of  $H_2$  needed for pressurization was 0.11 mol/kg of total material (sorbent + catalyst) in the column.

Figure 10 shows the effluent gas characteristics for step (a) of SERP for  $H_2$  production. It plots the average cumulative effluent gas  $H_2$  concentration (mol%) on a dry basis as a function of net  $H_2$  product gas quantity ( $H$ , mol/kg of total material in column). The plot also shows the average cumulative concentration of  $CH_4$  in the product  $H_2$ . The average concentrations of  $CO$  and  $CO_2$  in the product gas are less than 50 ppm. The quantity  $H$  is defined as the total amount of product  $H_2$  minus the amount of  $H_2$  used for pressurizing the reactor.

It may be seen from Figure 10 that the sorption-reaction step of the SERP concept at  $450^\circ C$  directly produces a substantial quantity of high purity  $H_2$  product ( $\geq 95$  mol%) with methane as the bulk impurity ( $< 5$  mol%) and trace quantities of carbon oxides impurities ( $< 50$  ppm). Obviously, the larger the purity of  $H_2$  in the product gas, the lower will be the  $H_2$  product quantity. The conversion of  $CH_4$  to  $H_2$  for any given value of  $H$  can be calculated by knowing the corre-



**Figure 10. Characteristics of  $H_2$ -enriched product effluent gas produced during sorption-reaction step of SERP concept.**

sponding amount of feed  $CH_4$  introduced into the reactor. The conversion is 82% when the net  $H_2$  product is 0.8 mol/kg and the  $H_2$  product purity is 96% (balance  $CH_4$  + trace amounts of  $CO$  and  $CO_2$ ).

Table 1 summarizes the performance of SERP concept for the experiment reported in this work and compares it with the performance of a conventional SMR reactor (without sorbent) for  $H_2$  production at 450°C. The same  $H_2O:CH_4$  ratio of the reactor feed gas and reaction pressure ( $P_R$ ) were used for calculating the performance of the conventional SMR reactor. It may be seen that the SERP concept at 450°C permits production of a much higher purity  $H_2$  product at a much larger  $CH_4$  to  $H_2$  conversion than the catalyst alone case at the same temperature. In particular, the  $H_2$  product gas from the SERP concept is essentially a mixture of  $H_2$  (> 95 mol%) and  $CH_4$  with trace amounts (ppm) of carbon oxides. The conventional SMR process at 450°C, on the other hand, produces an  $H_2$  product containing a much lower concentration of  $H_2$  (53 mol%) and a large quantity (13 mol%) of carbon oxide impurities. Thus, the subsequent purification of  $H_2$  by a PSA system is much easier and simpler for the SERP case.

Table 1 also shows that a reaction temperature of ~650°C is required by the catalyst alone case for matching the  $CH_4$  to  $H_2$  conversion of the present SERP case. The  $H_2$  product gas from the corresponding SMR reactor again contains a

moderate concentration of  $H_2$  (75.5 mol%) with a very large amount (20 mol%) of carbon oxide impurities.

The above results demonstrate that the proposed SERP concept can be used to directly produce a purer  $H_2$  stream with trace amounts of carbon oxide impurities at reaction pressure with high conversion of  $CH_4$  to  $H_2$ , while requiring a much lower reaction temperature than the conventional SMR process. The absence of bulk carbon oxide impurities in the  $H_2$  product stream by the SERP concept simplifies the subsequent  $H_2$  purification step by PSA compared to that required for the case of conventional SMR route for  $H_2$  production. For some refinery applications which do not require very high purity  $H_2$  gas, the subsequent  $H_2$  purification step can be completely eliminated by using the SERP concept for  $H_2$  production.

### Summary

A Sorption-Enhanced Reaction Process (SERP) concept is described that can be used to directly produce high purity (> 95 mol%)  $H_2$  product containing  $CH_4$  as the bulk impurity (< 5 mol%) and carbon oxides as trace impurities (~ 50 ppm) at the reaction pressure by steam methane reformation. The process allows high conversion of  $CH_4$  to  $H_2$  while operating at a much lower reaction temperature than that required by the conventional equilibrium controlled, endothermic SMR reactor. Thus, the SERP concept offers high potential for cost saving compared to the conventional catalytic SMR route of  $H_2$  production by removing the need for high-temperature reactor metallurgy and by reducing or eliminating the need for subsequent  $H_2$  product purification systems.

The SERP concept uses an admixture of a chemisorbent and a SMR catalyst in the reactor. The chemisorbent selectively removes the undesired reaction product ( $CO_2$ ) of the SMR reaction from the reaction zone and thus enhances the conversion of  $CH_4$  to  $H_2$  according to Le Chatelier's principle. It also decreases the  $CO$  concentration of the product gas. The chemisorbent is periodically regenerated by the principles of pressure swing adsorption (PSA). The steps of the cyclic SERP process are so designed that only a single unit operation is needed to carry out the reaction and the majority of the desired product purification.

A proprietary chemisorbent based on potassium carbonate promoted hydrotalcite is developed for use in the SERP for  $H_2$  production. The material reversibly chemisorbs  $CO_2$  at a temperature of 300–500°C in the presence of excess steam. The chemisorption isotherm of  $CO_2$  on the material is Type I by Brunauer classification. The material provides a substan-

**Table 1. Hydrogen Production by SERP and Conventional SMR Process**

	Product Purity on Dry Basis (mol%)	$CH_4$ Conversion (%)	$H_2$ Productivity (mol/kg)
SERP at 450°C and 55 psig $H_2O:CH_4 \approx 6:1$	96% $H_2$ + 4% $CH_4$ + < 50 ppm ( $CO + CO_2$ )	82	0.80
SMR at 450°C and 55 psig $H_2O:CH_4 \approx 6:1$	53% $H_2$ + 34% $CH_4$ + 13% ( $CO + CO_2$ )	28	—
SMR at 645°C and 55 psig $H_2O:CH_4 \approx 6:1$	75.5% $H_2$ + 4.4% $CH_4$ + 20.1% ( $CO + CO_2$ )	82	—

SI conversion:  $kPa = (psig + 14.7) \times 6.89$ .

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tial  $\text{CO}_2$  sorption capacity and it can be regenerated by lowering the superimposed partial pressure of  $\text{CO}_2$  over the sorbent. The kinetics of  $\text{CO}_2$  chemisorption and its desorption from the material is fast.

The SERP concept for  $\text{H}_2$  production by SMR is experimentally demonstrated using an admixture of the proprietary  $\text{CO}_2$  chemisorbent and a commercial SMR catalyst at a temperature of 450°C and a pressure of 55 psig (380.3 kPa). The reactor directly produced a 95+ mol% pure  $\text{H}_2$  stream containing 5 mol%  $\text{CH}_4$  and less than 50 ppm of carbon oxide impurities using a feed gas containing steam and methane in the ratio of 6:1. The  $\text{CH}_4$  to  $\text{H}_2$  conversion was 82%. A conventional SMR reactor operated at 450°C under equivalent feed gas conditions would produce a  $\text{H}_2$  product stream containing 53%  $\text{H}_2$ , 34%  $\text{CH}_4$ , and 13% carbon oxides with a  $\text{CH}_4$  to  $\text{H}_2$  conversion of only 28%. A temperature of ~650°C would be necessary for a conventional SMR reactor in order to match the  $\text{CH}_4$  to  $\text{H}_2$  conversion of the SERP concept operated at 450°C using the same feed gas conditions. The SMR reactor effluent in this case would consist of 5.5%  $\text{H}_2$ , 4.4%  $\text{CH}_4$ , and 20.1% carbon oxides.

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## Conclusion

CO<sub>2</sub> is sorbed from chemisorbent by N<sub>2</sub> purge to a product produced during the sorption-

process. The amount  $i$  in effluent gas

$y_i$  = gas phase mole fraction of component  $i$

$y'_i$  = feed gas mole fraction of component  $i$

$x$  = mol of  $\text{H}_2$  formed per mole of  $\text{CH}_4$  introduced in the batch SMR reactor.

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